



US009223218B2

(12) **United States Patent**
Vest et al.

(10) **Patent No.:** **US 9,223,218 B2**
(45) **Date of Patent:** ***Dec. 29, 2015**

(54) **PHOTOSENSITIVE RESIN LAMINATE AND THERMAL PROCESSING OF THE SAME**

USPC 430/306
See application file for complete search history.

(71) Applicant: **MacDermid Printing Solutions, LLC**,
Waterbury, CT (US)

(56) **References Cited**

(72) Inventors: **Ryan W. Vest**, Cumming, GA (US);
David A. Recchia, Smyrna, GA (US);
Timothy Gotsick, Acworth, GA (US)

U.S. PATENT DOCUMENTS

3,264,103	A	8/1966	Cohen et al.
3,265,765	A	8/1966	Holden et al.
3,867,153	A	2/1975	MacLachlan
4,264,705	A	4/1981	Allen
4,320,188	A	3/1982	Heinz et al.

(Continued)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

This patent is subject to a terminal disclaimer.

FOREIGN PATENT DOCUMENTS

EP	0 456 336	11/1991
EP	0 640 878	3/1995

(Continued)

(21) Appl. No.: **14/016,443**

Primary Examiner — Chanceity Robinson

(22) Filed: **Sep. 3, 2013**

(74) *Attorney, Agent, or Firm* — Carmody Torrance Sandak & Hennessy LLP

(65) **Prior Publication Data**

US 2014/0004466 A1 Jan. 2, 2014

Related U.S. Application Data

(62) Division of application No. 13/091,466, filed on Apr. 21, 2011, now Pat. No. 8,551,688.

(51) **Int. Cl.**

G03F 7/00	(2006.01)
G03F 7/26	(2006.01)
G03F 7/09	(2006.01)
G03F 7/34	(2006.01)
G03F 7/20	(2006.01)

(52) **U.S. Cl.**

CPC **G03F 7/26** (2013.01); **G03F 7/092** (2013.01);
G03F 7/202 (2013.01); **G03F 7/34** (2013.01);
B41M 2205/14 (2013.01)

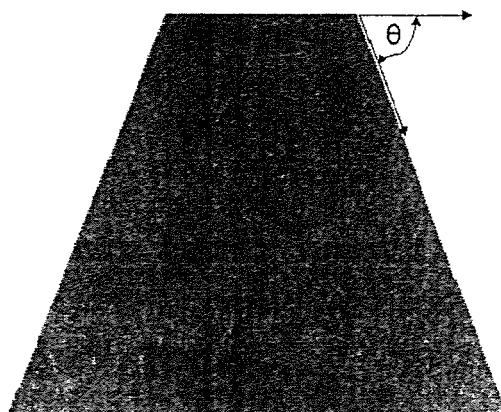
(58) **Field of Classification Search**

CPC G03F 7/20; G03F 1/003; B41M 1/04

(57) **ABSTRACT**

A method of developing a photocurable printing blank to produce a relief pattern comprising a plurality of relief dots having desired characteristics. The photocurable printing blank comprises a backing layer having at least one photocurable layer disposed thereon and a barrier layer disposed on the at least one photocurable layer. The method includes the steps of (1) placing a negative of a desired relief image on top of the barrier layer; (2) exposing the printing blank to actinic radiation through the barrier layer and negative to selectively crosslink and cure portions of the at least one photocurable layer, wherein the at least one photocurable layer is crosslinked and cured in the portions not covered by the negative, thereby creating the relief pattern; and (3) developing the printing blank to remove the barrier layer and uncured portions of the photocurable layer and reveal the relief pattern.

17 Claims, 4 Drawing Sheets



(56)

References Cited

U.S. PATENT DOCUMENTS

4,323,636	A	4/1982	Chen
4,323,637	A	4/1982	Chen et al.
4,369,246	A	1/1983	Chen et al.
4,423,135	A	12/1983	Chen et al.
4,427,759	A	1/1984	Gruetzmacher et al.
4,540,649	A	9/1985	Sakurai
4,622,088	A	11/1986	Min
5,135,827	A	8/1992	Bohm et al.
5,175,072	A	12/1992	Martens
5,223,375	A	6/1993	Berrier et al.
5,262,275	A	11/1993	Fan
5,279,697	A	1/1994	Peterson et al.
5,330,882	A	7/1994	Kawaguchi et al.
5,506,086	A	4/1996	Van Zoeren
5,925,500	A	7/1999	Yang

6,238,837	B1	5/2001	Fan	
6,773,859	B2	8/2004	Fan et al.	
7,122,295	B2	10/2006	Mengel et al.	
2004/0081908	A1	4/2004	Shimazu et al.	
2006/0063109	A1*	3/2006	Choi et al.	430/300
2009/0042138	A1	2/2009	Roberts et al.	
2011/0079158	A1	4/2011	Recchia	
2011/0081614	A1	4/2011	Recchia	
2012/0171620	A1*	7/2012	Bryant	430/306

FOREIGN PATENT DOCUMENTS

EP	1 239 329	9/2002
GB	1 366 769	9/1974
WO	01/18604	3/2001
WO	01/88615	11/2001

* cited by examiner

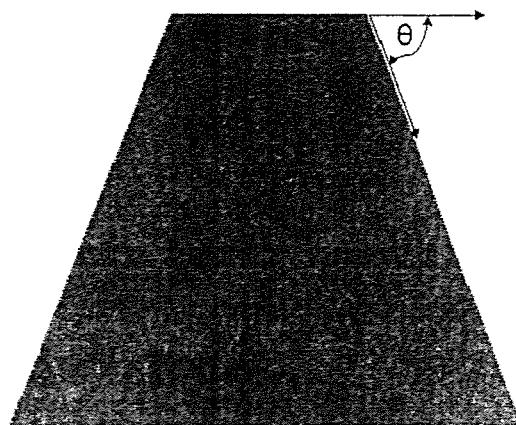


FIGURE 1

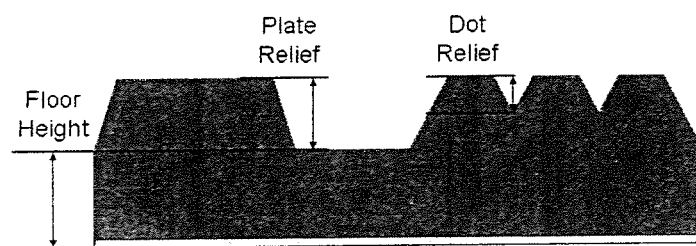


FIGURE 2

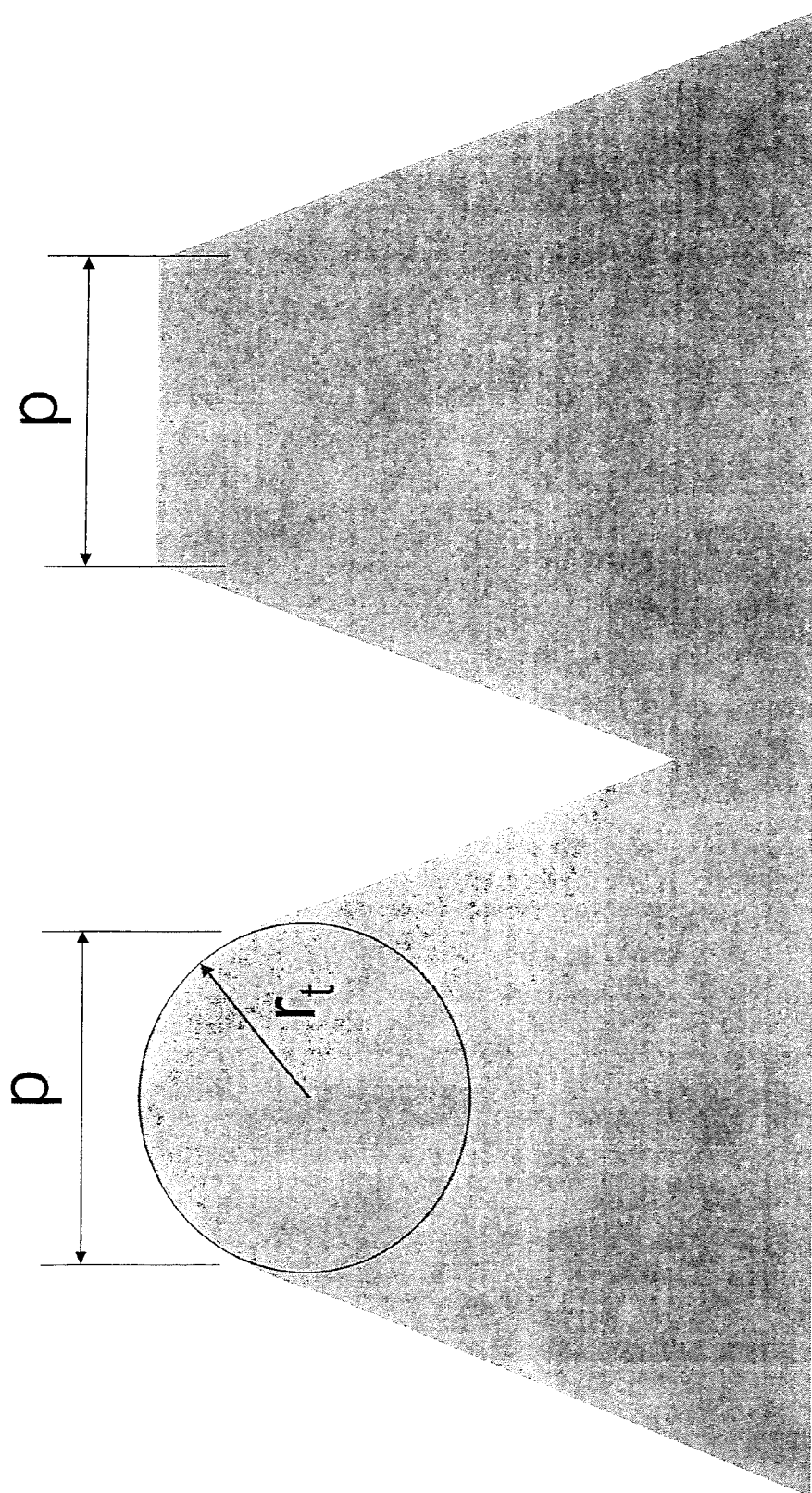


FIGURE 3

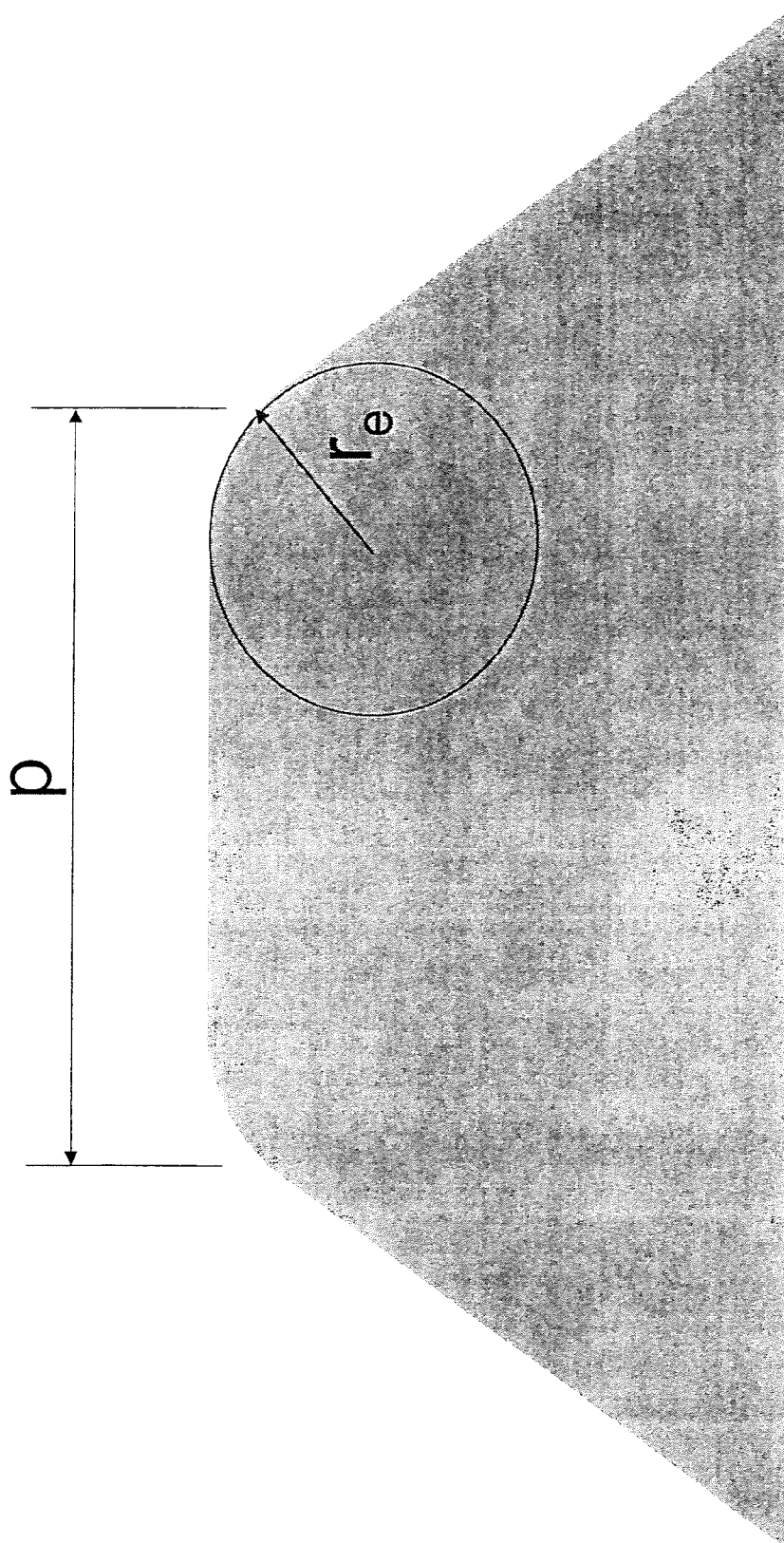


FIGURE 4

1

PHOTOSENSITIVE RESIN LAMINATE AND THERMAL PROCESSING OF THE SAME

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a divisional of application Ser. No. 13/091,466, filed Apr. 21, 2011, now pending, the subject matter of which is incorporated by reference in its entirety.

FIELD OF THE INVENTION

The present invention relates generally to methods of processing resin laminates to produce flexographic relief image printing elements for optimal printing.

BACKGROUND OF THE INVENTION

Flexographic printing plates are relief plates with image elements raised above open areas. Generally, the plate is somewhat soft, and flexible enough to wrap around a printing cylinder, and durable enough to print over a million copies. Such plates offer a number of advantages to the printer, based chiefly on their durability and the ease with which they can be made.

Flexography is commonly used for high-volume runs. Flexography is employed for printing on a variety of substrates such as paper, paperboard stock, corrugated board, films, foils and laminates. Newspapers and grocery bags are prominent examples. Coarse surfaces and stretch films can be economically printed only by means of flexography. Corrugated board generally includes a corrugating medium which is typically a layer of pleated or multi-grooved paperboard, called "flute", adjacent to a flat paper or paper-like layer called a "liner." A typical corrugated board construction comprises a flute layer sandwiched between two liner layers. Other embodiments may include multiple layers of flute and/or liner. The fluted interlayer provides structural rigidity to the corrugated board. Since corrugated board is used as packaging and formed into boxes and containers, the liner layer forming an exterior surface of the corrugated board is frequently printed with identifying information for the package. The exterior liner layer often has slight indentations due to the uneven support of the underlying flute layer.

A problem that may be encountered when printing on corrugated board substrates is the occurrence of a printing effect referred to as "fluting" (and which is also known as "banding" or "striping" or "washboarding"). Fluting may occur, when printing the liner on the exterior surface of the corrugated board, after the corrugated board has been assembled. The fluting effect is visible as regions of dark printing, i.e., bands of higher density, alternating with regions of light printing, i.e., bands of lighter density, that correspond to the underlying fluting structure of the corrugated board. The darker printing occurs where uppermost portions of the pleated innerlayer structure support the printing surface of the liner. The fluting effect can be apparent in areas of a printed image having tones or tint values where the inked areas represent a fraction of the total area as well as in areas of the printed image where the ink coverage is more complete. This fluting effect is typically more pronounced when printing with a flexographic printing element produced using a digital workflow process because of the shape of the dots produced by the digital process. Furthermore, increasing the printing pressure does not eliminate fluting, and the increased pressure can cause damage to the corrugated board substrate. There-

2

fore, other methods are needed to reduce fluting when printing on corrugated board substrates.

A typical flexographic printing plate as delivered by its manufacturer is a multilayered article comprising, in order, a backing, or support layer; one or more unexposed photocurable layers; optionally a protective layer or slip film; and often a protective cover sheet.

The support sheet or backing layer lends support to the plate. The support sheet, or backing layer, can be formed from a transparent or opaque material such as paper, cellulose film, plastic, or metal. Preferred materials include sheets made from synthetic polymeric materials such as polyesters, polystyrene, polyolefins, polyamides, and the like. Generally the most widely used support layer is a flexible film of polyethylene terephthalate. The support sheet can optionally comprise an adhesive layer for more secure attachment to the photocurable layer(s). Optionally, an antihalation layer may also be provided between the support layer and the one or more photocurable layers. The antihalation layer is used to minimize halation caused by the scattering of UV light within the non-image areas of the photocurable resin layer.

The photocurable layer(s) can include any of the known photopolymers, monomers, initiators, reactive or non-reactive diluents, fillers, and dyes. The term "photocurable" refers to a composition which undergoes polymerization, cross-linking, or any other curing or hardening reaction in response to actinic radiation with the result that the unexposed portions of the material can be selectively separated and removed from the exposed (cured) portions to form a three-dimensional or relief pattern of cured material. Preferred photocurable materials include an elastomeric compound, an ethylenically unsaturated compound having at least one terminal ethylene group, and a photoinitiator. Exemplary photocurable materials are disclosed in European Patent Application Nos. 0 456 336 A2 and 0 640 878 A1 to Goss, et al., British Patent No. 1,366,769, U.S. Pat. No. 5,223,375 to Berrier, et al., U.S. Pat. No. 3,867,153 to MacLahan, U.S. Pat. No. 4,264,705 to Allen, U.S. Pat. Nos. 4,323,636, 4,323,637, 4,369,246, and 4,423,135 all to Chen, et al., U.S. Pat. No. 3,265,765 to Holden, et al., U.S. Pat. No. 4,320,188 to Heinz, et al., U.S. Pat. No. 4,427,759 to Gruetzmacher, et al., U.S. Pat. No. 4,622,088 to Min, and U.S. Pat. No. 5,135,827 to Bohm, et al., the subject matter of each of which is herein incorporated by reference in its entirety. More than one photocurable layer may be used.

Photocurable materials generally cross-link (cure) and harden through radical polymerization in at least some actinic wavelength region. As used herein, actinic radiation is radiation capable of polymerizing, crosslinking or curing the photocurable layer. Actinic radiation includes, for example, amplified (e.g., laser) and non-amplified light, particularly in the UV and violet wavelength regions. One commonly used source of actinic radiation is a mercury arc lamp, although other sources are generally known to those skilled in the art.

The slip film is a thin layer, which protects the photopolymer from dust and increases its ease of handling. In a conventional ("analog") plate making process, the slip film is transparent to UV light. In this process, the printer peels the cover sheet off the printing plate blank, and places a negative on top of the slip film layer. The plate and negative are then subjected to flood-exposure by LTV light through the negative. The areas exposed to the light cure, or harden, and the unexposed areas are removed (developed) to create the relief image on the printing plate.

In a "digital" or "direct to plate" plate making process, a laser is guided by an image stored in an electronic data file, and is used to create an in situ negative in a digital (i.e., laser

ablatable) masking layer, which is generally a slip film which has been modified to include a radiation opaque material. Portions of the laser ablatable layer are then ablated by exposing the masking layer to laser radiation at a selected wavelength and power of the laser. Examples of laser ablatable layers are disclosed, for example, in U.S. Pat. No. 5,925,500 to Yang, et al., and U.S. Pat. Nos. 5,262,275 and 6,238,837 to Fan, the subject matter of each of which is herein incorporated by reference in its entirety.

After imaging, the photosensitive printing element is developed to remove the unpolymerized portions of the layer of photocurable material and reveal the crosslinked relief image in the cured photosensitive printing element. Typical methods of development include washing with various solvents or water, often with a brush. Other possibilities for development include the use of an air knife or heat plus a blotter (i.e., thermal development). Thermal development has the advantage of not requiring an additional drying step after development and thus provides the ability to go more quickly from plate to press.

Thermal development processes work by processing photopolymer printing plates using heat; the differential melting temperature between cured and uncured photopolymer is used to develop the latent image. The basic parameters of this process are known, as described in U.S. Pat. Nos. 7,122,295, 6,773,859, 5,279,697, 5,175,072 and 3,264,103 and in WO 01/88615, WO 01/18604, and EP 1239329, the teachings of each of which are incorporated herein by reference in their entirety. These processes allow for the elimination of development solvents and the lengthy plate drying times needed to remove the solvent. The speed and efficiency of these processes allow for their use in the manufacture of flexographic plates for printing newspapers and other publications where quick turnaround times and high productivity are important.

In order for printing plates to be thermally developable, the composition of the photopolymer must be such that there exists a substantial difference in the melt temperature between the cured and uncured polymer. It is precisely this difference that allows the creation of an image in the photopolymer when heated. The uncured photopolymer (i.e., the portions of the photopolymer not contacted with actinic radiation) melts and/or substantially softens while the cured photopolymer remains solid and intact at the temperature chosen. Thus, the difference in melt temperature allows the uncured photopolymer to be selectively removed, thereby creating the desired image.

Thereafter, uncured photopolymer can be softened and/or melted and removed. In most instances, the heated printing element is contacted with an absorbent material that absorbs or otherwise removes the softened and/or melted uncured photopolymer. This removal process is generally referred to as "blotting."

The resulting surface, after development, has a relief pattern that reproduces the image to be printed and which typically includes both solid areas and patterned areas comprising a plurality of relief dots. After the relief image is developed, the relief image printing element may be mounted on a press and printing commenced.

The shape of the dots and the depth of the relief, among other factors, affect the quality of the printed image. It is very difficult to print small graphic elements such as fine dots, lines and even text using flexographic printing plates while maintaining open reverse text and shadows. In the lightest areas of the image (commonly referred to as highlights) the density of the image is represented by the total area of dots in a halftone screen representation of a continuous tone image. For Amplitude Modulated (AM) screening, this involves shrinking a

plurality of halftone dots located on a fixed periodic grid to a very small size, the density of the highlight being represented by the area of the dots. For Frequency Modulated (FM) screening, the size of the halftone dots is generally maintained at some fixed value, and the number of randomly or pseudo-randomly placed dots represent the density of the image. In both cases, it is necessary to print very small dot sizes to adequately represent the highlight areas.

Maintaining small dots on flexographic plates can be very difficult due to the nature of the platemaking process. In digital platemaking processes that use a UV-opaque mask layer, the combination of the mask and UV exposure produces relief dots that have a generally conical shape. The smallest of these dots are prone to being removed during processing, which means no ink is transferred to these areas during printing (the dot is not "held" on plate and/or on press). Alternatively, if the dot survives processing they are susceptible to damage on press. For example small dots often fold over and/or partially break off during printing causing either excess ink or no ink to be transferred.

Furthermore, photocurable resin compositions typically cure through radical polymerization, upon exposure to actinic radiation. However, the curing reaction can be inhibited by molecular oxygen, which is typically dissolved in the resin compositions, because the oxygen functions as a radical scavenger. It is therefore desirable for the dissolved oxygen to be removed from the resin composition before image-wise exposure so that the photocurable resin composition can be more rapidly and uniformly cured.

Various methods of removing dissolved oxygen have been developed for use in the art. For example, the removal of dissolved oxygen can be accomplished by placing the photosensitive resin plate in an atmosphere of inert gas, such as carbon dioxide gas or nitrogen gas, before exposure in order to displace the dissolved oxygen. A noted drawback to this method is that it is inconvenient and cumbersome and requires a large space for the apparatus. In addition, as discussed in more detail below, this approach has not been found to be particularly effective in digital printing elements that are thermally developed.

Another approach involves subjecting the plates to a preliminary exposure (i.e., "bump exposure") of actinic radiation. During bump exposure, a low intensity "pre-exposure" dose of actinic radiation is used to sensitize the resin before the plate is subjected to the higher intensity main exposure dose of actinic radiation. The bump exposure is applied to the entire plate area and is a short, low dose exposure of the plate that reduces the concentration of oxygen, which inhibits photopolymerization of the plate (or other printing element) and aids in preserving fine features (i.e., highlight dots, fine lines, isolated dots, etc.) on the finished plate. However, the pre-sensitization step can also cause shadow tones to fill in, thereby reducing the tonal range of the halftones in the image.

The bump exposure requires specific conditions that are limited to only quench the dissolved oxygen, such as exposing time, irradiated light intensity and the like. In addition, a selective preliminary exposure, as discussed for example in U.S. Pat. Publication No. 2009/0043138 to Roberts et al., the subject matter of which is herein incorporated by reference in its entirety, has been proposed.

Other efforts have involved special plate formulations alone or in combination with the bump exposure, such as in U.S. Pat. No. 5,330,882 to Kawaguchi, the subject matter of which is herein incorporated by reference in its entirety, which suggests the use of a separate dye that is added to the resin to absorb actinic radiation at wavelengths at least 100 nm removed from the wavelengths absorbed by the main

photoinitiator. U.S. Pat. No. 4,540,649 to Sakurai, incorporated herein by reference in its entirety, describes a photopolymerizable composition that contains at least one water soluble polymer, a photopolymerization initiator and a condensation reaction product of N-methylol acrylamide, N-methylol methacrylamide, N-alkyloxymethyl acrylamide or N-alkyloxymethyl methacrylamide and a melamine derivative, which, according to the inventors, eliminates the need for pre-exposure conditioning and produces a chemically and thermally stable plate.

However all of these methods are still deficient in producing a relief image printing element having a superior dot structure, especially when designed for printing corrugated board substrates. In addition, all of the methods described above have also not been shown to produce a relief image printing element having superior dot structure when the relief image is subjected to a thermal development step.

When developing in solvent, the main consideration is whether or not the solvent can swell and disperse/dissolves the uncured photopolymer and associated barrier layers, in combination with the appropriate mechanical agitation, resulting in a clean printing plate free of contaminants, surface defects, or other unwanted solvent-based phenomenon common to the platemaking industry.

In contrast, developing plates thermally sometimes requires other considerations. Digital plates, when exposed by conventional means (i.e., in air) have previously been believed to be interchangeable whether subject to a solvent development process or a thermal development process, using the same base resin formulation. Analog thermal has shown itself to be more challenging, oftentimes requiring the use of a novel slip film or unique properties to the resin itself, such as very high melt flow.

Thus, there is a need for an improved process for preparing relief image printing elements.

There is also a need for an improved relief image printing element that comprises an improved relief structure including printing dots that are configured for superior printing performance on various substrates.

The present invention relates generally to a digital plate with dots of a controlled architecture beneficial to printing (i.e., flat top, steep shoulders).

The present invention also provides a means for exposing and processing an analog plate via the same exposure technique.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide an improved method of thermally developing digital relief image printing elements.

It is another object of the present invention to provide an improved method of thermally developing analog relief image printing elements.

It is another object of the present invention to provide an improved method of developing relief image printing plate that produces printing dots having a flat top and steep shoulders.

It is still another object of the present invention to provide a method of imaging and developing relief image printing elements that provides a good result when printing on corrugated board substrates.

It is another object of the present invention to produce a relief image printing plate that reduces print fluting when printing on corrugated board substrates.

It is another object of the present invention to create a relief image printing element that comprises printing dots having a

superior dot structure in terms of print surface, edge definition, shoulder angle, depth and dot height.

It is another object of the present invention to provide a dot shape and structure on the printing element that is highly resistant to print fluting.

It is still another object of the present invention to control the surface roughness of the print surface of the relief image printing element.

The inventors here have discovered that a characteristic of plates processed by thermal means is higher surface roughness of both solid areas and the tops of dots, as well as the floor of the plate. This is due to the fact that 'blotting' is incapable of removing all of the photopolymer during thermal processing. There is always some small amount of residual polymer left on the plate, both on the relief elements and on the plate's floor. The texture of the blotter material is typically transferred into this remnant photopolymer. In the floor areas of the plate, this distinctive pattern has only cosmetic effect. However, on the relief elements, this texture can be problematic. If the roughness of the texture is excessive, it can affect print quality by actually transferring the pattern to the surface being printed, resulting in qualitative print defects often described as mottling or pinholing, and the quantitative print defect of reduced solid ink density (SID). These defects generally degrade the quality of the printed articles made from plates with excessive roughness, reducing the vibrancy of colors and making it difficult to achieve consistent color reproduction.

Some degree of plate surface roughness can be beneficial to print performance, but excessive surface roughness can have the above-described negative effects. The definition of 'excessive' plate surface roughness varies depending upon many factors, including the substrate printed, the ink characteristics, and the amount of ink used on each image. Generally, the inventors have found that plate surface roughness of less than 2000 nm (R_a) is required to achieve good and uniform solid ink coverage, with plate surface roughness of less than 1200 nm preferred, and plate surface roughness of less than 800 nm most preferred.

To these ends, in a preferred embodiment, the present invention relates generally to a method of developing a photocurable printing blank to produce a relief pattern comprising a plurality of relief dots, wherein the photocurable printing blank comprises a backing layer having at least one photocurable layer disposed thereon, a barrier layer disposed on the at least one photocurable layer, and a laser ablatable mask layer disposed on top of the barrier layer, the method comprising the steps of:

- a) imaging the at least one photocurable layer by selectively ablating the laser ablatable mask layer to create an image on the surface of the photocurable printing blank;
- b) exposing the printing blank to actinic radiation through the mask layer and the barrier layer to one or more sources of actinic radiation to selectively crosslink and cure portions of the at least one photocurable layer, wherein the at least one photocurable layer is crosslinked and cured in the portions not covered by the mask layer, thereby creating the relief pattern; and
- c) developing the printing blank to remove the laser ablated mask layer, the barrier layer and uncured portions of the photocurable layer and reveal the relief pattern;

wherein the presence of the barrier layer produces printing dots having desired characteristics and wherein the barrier layer has an oxygen diffusion coefficient of less than about $6.9 \times 10^{-9} \text{ m}^2/\text{sec}$ and an optical transparency of at least 50%.

In another preferred embodiment, the present invention relates generally to a method of developing a photocurable

printing blank to produce a relief pattern comprising a plurality of relief dots, wherein the photocurable printing blank comprises a backing layer having at least one photocurable layer disposed thereon and a barrier layer on the at least one photocurable layer, the method comprising the steps of:

- a) placing a negative of a desired relief image on top of the barrier layer;
- b) exposing the printing blank to actinic radiation through the barrier layer and negative to selectively crosslink and cure the at least one photocurable layer, wherein the at least one photocurable layer is crosslinked and cured in the areas that are not covered by the negative, thereby creating the desired relief image; and
- c) developing the printing blank to remove the barrier layer and the uncured portions of the photocurable layer and reveal the desired relief image;

wherein the presence of the barrier layer results in the plurality of printing dots having desired characteristics and wherein the barrier layer has an oxygen diffusion coefficient of less than about $6.9 \times 10^{-9} \text{ m}^2/\text{sec}$ and an optical transparency of at least 50%.

BRIEF DESCRIPTION OF THE DRAWINGS

For a fuller understanding of the invention, reference is had to the following description taken in connection with the accompanying figures, in which:

FIG. 1 depicts the measurement of the dot shoulder angle θ .

FIG. 2 depicts relief image definitions.

FIG. 3 depicts a means of characterizing the planarity of a dot's printing surface where p is the distance across the dot top and r_t is the radius of curvature across the surface of the dot.

FIG. 4 depicts a flexo dot and its edge, where p is the distance across the dot top. This is used in the characterization of edge sharpness, r_e/p , where r_e is the radius of curvature at the intersection of the shoulder and the top of the dot.

DETAILED DESCRIPTION OF THE INVENTION

The inventors of the present invention have found that the shape and structure of a printing dot has a profound impact on the way it prints. This is especially true in digital relief image printing elements. The inventors of the present invention have also determined that there are special considerations which must be addressed when using thermal development processes to provide a relief surface that includes relief printing dots having flat tops and steep shoulders.

The inventors of the present invention have discovered that there is an advantage to reducing the impact of oxygen inhibition during plate exposure while simultaneously maintaining the physical properties necessary to produce high quality thermally processed printing plates.

The present invention relates generally to the application of a barrier layer onto (i) the surface of the photopolymer between the ablatable mask layer and the photopolymer layer or (ii) the surface of the photopolymer layer between the photopolymer layer and the phototool negative. The plate is then processed to remove uncured photopolymer, thereby producing a relief printing plate. The barrier layer's function is to serve as a oxygen barrier which allows for altering of the shape of the formed dots on the printing plate. The result of the use of this barrier layer is the advantageous control of the curing mechanism such that the following occurs:

- 1) Dots are formed without the restricting effect of oxygen inhibition, resulting in flat tops and steep shoulder angles;

- 2) The curing rate is controlled to the point that optimum reverse depths are maintained and shoulder angles are not excessively broadened;
- 3) The barrier layer minimizes the creation of excessive surface roughness during thermal processing; and
- 4) The barrier layer allows for more efficient thermal processing of a printing form than currently existing plate constructions.

The present invention utilizes the aforementioned advantages of the barrier layer as an oxygen barrier and combines them with the surprising discovery that plates comprising a barrier layer perform better in print studies than standard processed plates as well as those exposed in inert gas media, showing reduced dot gain and cleaner solids and reverse print.

In a preferred embodiment, the present invention relates generally to a method of developing a photocurable printing blank to produce a relief pattern comprising a plurality of relief dots, wherein the photocurable printing blank comprises a backing layer having at least one photocurable layer disposed thereon, a barrier layer disposed on the at least one photocurable layer and a laser ablatable mask layer disposed on top of the barrier layer, the method comprising the steps of:

- a) imaging the at least one photocurable layer by selectively ablating the laser ablatable mask layer to create an image on the surface of the photocurable printing blank;
- b) exposing the at least one photocurable layer to actinic radiation through the barrier layer and mask layer to one or more sources of actinic radiation to selectively crosslink and cure portions of the at least one photocurable layer, wherein the at least one photocurable layer is crosslinked and cured in the portions not covered by the mask layer, thereby creating the relief pattern; and
- c) developing the printing blank to remove the laser ablated mask layer, the barrier layer, and uncured portions of the photocurable layer and reveal the relief pattern;

wherein the presence of the barrier layer produces printing dots having desired geometric parameters and wherein the barrier layer has an oxygen diffusion coefficient of less than about $6.9 \times 10^{-9} \text{ m}^2/\text{sec}$ and an optical transparency of at least 50%.

The desired geometric parameters of the printing dots are typically one or more of steep shoulder angles, planarity of the dot surface, sufficient depth of relief between the dots, sharpness of the edge at the point where the dot top transitions to the dot shoulder, low surface roughness and combinations thereof. One can manipulate the resultant shape of the printing dots to optimize printing by utilizing the methods described herein.

The inventors of the present invention have found that a particular set of geometric characteristics define a flexo dot shape that yields superior printing performance. These geometric parameters include, but are not limited to, (1) planarity of the dot surface; (2) shoulder angle of the dot; (3) depth of relief between the dots; and (4) sharpness of the edge at the point where the dot top transitions to the dot shoulder. These geometric parameters are described in more detail in related patent application Ser. No. 12/571,523 to Recchia and Ser. No. 12/660,451 to Recchia et al., the subject matter of each of which is herein incorporated by reference in its entirety. However the particular use of these geometric parameters in optimizing print quality of printing dots produced in thermally development processes has not been previously been investigated.

Firstly, the angle of the dot shoulder has been found to be a good predictor of print performance. The dot shoulder is defined as shown in FIG. 1 as the angle θ formed by the dot's top and side. At the extreme, a vertical column would have a

90° shoulder angle, but in practice most flexo dots have an angle that is considerable lower, often nearer 45° than 90°.

The shoulder angle can vary depending on the size of the dots as well. Small dots, for example in the 1-15% range, may have large shoulder angles, while larger dots, for example greater than about 15% dots may exhibit smaller shoulder angles. It is desirable for all dots to have the largest shoulder angle possible. In one embodiment, the desired characteristics comprise steep shoulder angles and the shoulder angle of each of the plurality of dots is such that the overall shoulder angle is greater than about 50°, preferably greater than about 70°.

There are two competing geometric constraints on shoulder angle—dot stability and impression sensitivity. A large shoulder angle minimizes impression sensitivity and gives the widest operating window on press, but at the expense of dot stability and durability. In contrast, a lower shoulder angle improves dot stability but makes the dot more sensitive to impression on press. As used herein, dot shoulder angle means the angle formed by the intersection of a horizontal (or parallel to the dot top, depending on the shape of the dot's tip) line tangential to the top of the dot and a line representing the adjacent dot side wall.

In another embodiment, the desired characteristics comprise planarity of the dot surface. The planarity of the top of a dot can be measured as the radius of curvature across the top surface of the dots, r_t , as shown in FIG. 3. Preferably, the top surface of the dot has a planarity, where the radius of curvature of the dot top is greater than the total thickness of the at least one layer of photocurable material, more preferably twice the thickness of the at least one layer of photocurable material, and most preferably, more than three times the total thickness of the photopolymer layer. A planar dot surface is preferred throughout the tonal range. Most preferred are planar dot surfaces, even on dots in the highlight range (i.e., 0-10% tonal).

In still another embodiment, the desired characteristic of the printing dots is low surface roughness and the surface roughness of the top of the plurality of relief printing dots is less than about 2000 nm, preferably less than about 1250 nm, and most preferably less than 800 nm.

In another embodiment, the desired characteristic of the printing dots is sufficient depth of relief between the dots, and a dot relief of printing element is greater than about 9% of the overall plate relief, preferably greater than about 12% of the overall plate relief. Plate relief is expressed as the distance between the floor of the plate and the top of a solid relief surface, as shown in FIG. 2. For example, a 0.125 inch thick plate is typically made so as to have an 0.040 inch relief. However, the plate relief is typically much larger than the relief between dots in tone patches (i.e., the "dot relief"), which is a result of the close spacing of the dots in tonal areas. The low relief between dots in tonal areas means that the dots are structurally well-supported, but can cause problems during printing as ink builds up on the plate and eventually fills in the areas between dots, causing dot bridging or dirty print. The inventors have found that deeper dot relief can reduce this problem significantly, leading to longer print runs with less operator interference, a capability that is often called "cleaner printing."

In another embodiment, the desired characteristic is sharpness of the edge at the point where the dot top transitions to the dot shoulder. It is generally preferred that the dot edges be sharp and defined. These well-defined dot edges better separate the "printing" portion from the "support" portion of the dot, allowing for a more consistent contact area between the dot and the substrate during printing. Edge sharpness can be

defined as the ratio of r_e , the radius of curvature (at the intersection of the shoulder and the top of the dot) to p , the width of the dot's top or printing surface, as shown in FIG. 4. For a truly round-tipped dot, it is difficult to define the exact printing surface because there is not really an edge in the commonly understood sense, and the ratio of $r_e:p$ can approach 50%. In contrast, a sharp-edged dot would have a very small value of r_e , and $r_e:p$ would approach zero. In practice, an $r_e:p$ of less than 5% is preferred, with an $r_e:p$ of less than 2% being most preferred.

A wide range of materials can serve as the barrier layer. Four qualities that the inventors have identified in producing effective barrier layers include optical transparency, low thickness, oxygen transport inhibition and the ability to preferentially develop away the barrier layer using solvents or heat. Oxygen transport inhibition is measured in terms of a low oxygen diffusion coefficient. As noted, the oxygen diffusion coefficient of the oxygen barrier membrane is typically less than about 6.9×10^{-9} m²/sec, more preferably less than about 6.9×10^{-10} m²/sec, and most preferably less than about 6.9×10^{-11} m²/sec.

The most preferred oxygen barrier layer are clear films that minimize light scattering. Examples of materials which are suitable for use as the barrier layer include polyamides, polyvinyl alcohol, hydroxyalkyl cellulose, polyvinyl pyrrolidone, copolymers of ethylene and vinyl acetate, amphoteric interpolymers, cellulose acetate butyrate, alkyl cellulose, butyral, cyclic rubbers, and combinations of one or more of the foregoing.

The barrier layer should be as thin as possible. Barrier layer thicknesses between about 1 and 100 microns are preferred, with thickness of between about 1 and about 20 microns being most preferred.

The barrier layer needs to have a sufficient optical transparency so that the membrane will not detrimentally absorb or deflect the actinic radiation used to expose the photosensitive printing blank. As such it is preferable that the barrier layer have an optical transparency of at least 50%, most preferably at least 75%.

The barrier layer needs to be sufficiently impermeable to oxygen diffusion so that it can effectively limit diffusion of oxygen into the photocurable layer during exposure to actinic radiation. The inventors herein have determined that the barrier layer materials noted above in the thicknesses noted above will substantially limit the diffusion of oxygen into the photocurable layer when used as described herein.

Suitable thermal development processes are generally well known to those skilled in the art. In one embodiment, the thermal development step comprises the steps of:

- a) softening non-crosslinked polymer on the imaged and exposed surface of the printing element by contacting the imaged and exposed surface with an absorbent layer capable of absorbing non-crosslinked portions of the at least one layer of photocurable material when it has been heated to a temperature of between 40° and 200° C.,
- b) heating said at least one layer of photocurable material to a temperature of between 40° and 200° C. and allowing the non-crosslinked portions of the at least one layer of photocurable material in contact with the absorbent layer to be absorbed by said absorbent layer, and
- c) removing said absorbent layer containing the non-crosslinked portion of the at least one photocurable layer, whereby the relief pattern is revealed.

Suitable solvent development materials and techniques are also known in the art.

In addition, the barrier layer can be used in an analog construction wherein a barrier layer is applied to a photopoly-

11

mer resin layer. A negative is then placed upon the barrier layer, and the platemaking occurs via standard analog platemaking practices.

More specifically, in another preferred embodiment, the present invention relates generally to a method of developing a photocurable printing blank to produce a relief pattern comprising a plurality of relief dots, wherein the photocurable printing blank comprises a backing layer having at least one photocurable layer disposed thereon, and a barrier layer on the at least one photocurable layer, the method comprising the steps of:

- a) placing a negative of a desired relief image on top of the barrier layer;
- b) exposing the at least one photocurable layer to actinic radiation through the barrier layer and negative to selectively crosslink and cure the at least one photocurable layer, wherein the at least one photocurable layer is crosslinked and cured in the areas that are not covered by the negative, thereby creating the desired relief image; and

- c) developing the printing blank to remove the barrier layer and the uncured portions of the photocurable layer and reveal the desired relief image;

wherein the presence of the barrier layer results in the plurality of printing dots having desired characteristics and wherein the barrier layer has an oxygen diffusion coefficient of less than $6.9 \times 10^{-9} \text{ m}^2/\text{sec}$ and an optical transparency of at least 50%.

Finally, once the plates have been subjected to development, the relief image printing element is mounted on a printing cylinder of a printing press and printing is commenced.

Thus, it can be seen that the method of making the relief image printing element described herein produces a relief image printing element having a relief pattern comprising relief dots to be printed that are configured for optimal print performance. In addition, through the method described herein, it is possible to make thermally developed plates, both digital and analog that have optimized geometric characteristics of the relief dots in the resulting relief image to produce a desired result.

What is claimed is:

1. A method of developing a photocurable printing blank to produce a relief pattern comprising a plurality of relief printing dots, wherein the photocurable printing blank comprises a backing layer having at least one photocurable layer disposed thereon and a barrier layer disposed on at least one photocurable layer, the method comprising the steps of:

- a) placing a negative of a desired relief image on top of the barrier layer;
- b) exposing the printing blank to actinic radiation through the barrier layer and negative to selectively crosslink and cure the at least one photocurable layer, wherein the at least one photocurable layer is crosslinked and cured in the areas that are not covered by the negative, thereby creating the desired relief image; and
- c) developing the printing blank to remove the barrier layer and the uncured portions of the photocurable layer and reveal the relief pattern;

wherein the barrier layer has an oxygen diffusion coefficient of less than $6.9 \times 10^{-9} \text{ m}^2/\text{sec}$ and an optical transparency of at least 50%.

2. The method according to claim 1, wherein the plurality of relief printing dots have one or more characteristics selected from:

12

a) steep shoulder angles, wherein the shoulder angle of each of the plurality of relief printing dots is such that the overall shoulder angle is greater than about 50° ;

b) planarity of a top surface of the relief printing dots, wherein the planarity of the top surface of the relief printing dots is such that the radius of curvature of the top surface of the relief printing dots, r_p , is greater than the total thickness of the at least one layer of photocurable material;

c) sufficient depth of relief between the relief printing dots, wherein the depth of relief between the relief printing dots is greater than about 9% of the overall plate relief;

d) edge sharpness of the relief printing dots, wherein the edge sharpness of the relief printing dots, defined as a ratio of the radius of curvature at the intersection of the shoulder and the top surface of the relief printing dot, (r_e) to the width of the top surface of the relief printing dot (p) is less than 5%; and

e) low surface roughness, wherein the surface roughness of the top surface of the plurality of relief printing dots is less than about 2000 nm.

3. The method according to claim 2, wherein the at least one characteristic comprises steep shoulder angles, wherein the shoulder angle of each of the plurality of relief printing dots is such that the overall shoulder angle is greater than about 50° .

4. The method according to claim 3, wherein the shoulder angle of each of the plurality of relief printing dots is such that overall shoulder angle is greater than about 70° .

5. The method according to claim 2, wherein the at least one characteristic comprises planarity of the top surface of the relief printing dots, wherein the planarity of the top surface of the relief printing dots is such that the radius of curvature of the top surface of the relief printing dots, r_p , is greater than the total thickness of the at least one layer of photocurable material.

6. The method according to claim 2, wherein the at least one characteristic comprises low surface roughness, wherein the surface roughness of the top surface of the plurality of relief printing dots is less than about 2000 nm.

7. The method according to claim 6, wherein the surface roughness of the top surface of the plurality of relief printing dots is less than about 800 nm.

8. The method according to claim 2, wherein the at least one characteristic comprises sufficient depth of relief between the relief printing dots, wherein the depth of relief between the relief printing dots is greater than about 9% of the overall plate relief.

9. The method according to claim 8, wherein the depth of relief between the relief printing dots is greater than about 12% of the overall plate relief.

10. The method according to claim 2, wherein the at least one characteristic comprises edge sharpness of the relief printing dots, wherein the ratio of $r_e:p$ is less than 5%.

11. The method according to claim 10, wherein the ratio of $r_e:p$ is less than 2%.

12. The method according to claim 1, wherein the barrier layer is selected from the group consisting of polyamides, polyvinyl alcohol, hydroxyalkyl cellulose, polyvinyl pyrrolidinone, copolymers of ethylene and vinyl acetate, amphoteric interpolymers, cellulose acetate butyrate, alkyl cellulose, butyral, cyclic rubbers, and combinations of one or more of the foregoing.

13. The method according to claim 1, wherein the barrier layer has a thickness of between about 1 and 100 microns.

14. The method according to claim 13, wherein the barrier layer has a thickness of between about 1 and 20 microns.

15. The method according to claim 1, wherein the barrier layer has an optical transparency of at least about 75%.

16. The method according to claim 1, wherein the step of developing the printing blank comprises:

- a) softening non-crosslinked polymer on the imaged and exposed surface of the printing blank by contacting the image and exposed surface with an absorbent layer capable of absorbing non-crosslinked portions of the at least one photocurable layer when it has been heated to a temperature of between 40° and 200° C.,
- b) heating said at least one layer of photocurable material to a temperature of between 40° and 200° C and allowing the non-crosslinked portions of the at least one photocurable layer in contact with the absorbent layer to be absorbed by said absorbent layer, and
- c) removing said absorbent layer containing the non-crosslinked portion of the at least one photocurable layer, whereby the relief pattern is revealed.

17. The method according to claim 1, wherein the printing blank is not imaged in an inert environment.

* * * * *